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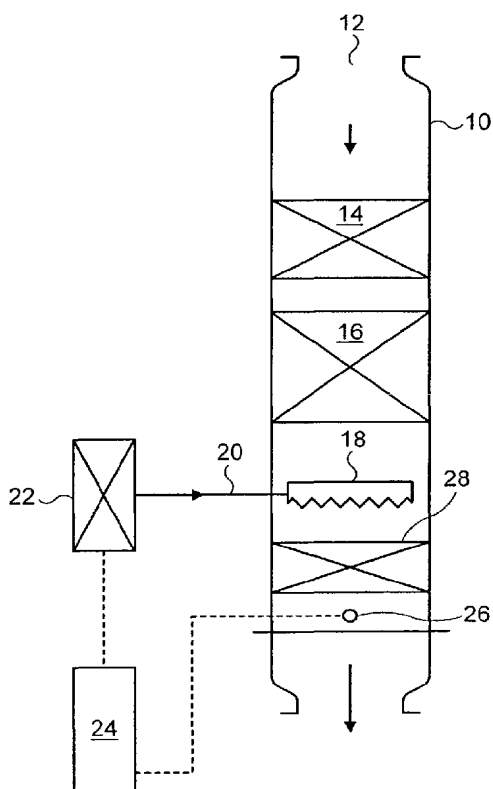
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(54) Title: GAS TREATMENT USING NO<sub>x</sub>-SPECIFIC REACTANT



(57) Abstract: A process for treating gas containing a NO<sub>x</sub>-specific reactant or NO<sub>x</sub> by contacting the gas with a solid absorbent comprises : removing the NO<sub>x</sub>-specific reactant from the gas using a solid absorbent comprising a nitroxy salt; or removing NO<sub>x</sub> from the gas using a solid absorbent comprising a basic material and intermittently regenerating the absorbent by the action of a NO<sub>x</sub>-specific reactant and stopping the action of the NO<sub>x</sub>-specific reactant while the absorbent contains nitroxy salt thereby substantially preventing slip of NO<sub>x</sub>-specific reactant. The invention also comprises an exhaust system (10) for an international combustion engine including a NO<sub>x</sub>-trap (28), means (18) for injecting a NO<sub>x</sub>-specific reactant or a precursor of a NO<sub>x</sub>-specific reactant upstream of the NO<sub>x</sub> trap (28), whereby NO<sub>x</sub> stored on the NO<sub>x</sub> trap is reduced by the NH<sub>3</sub> and the NO<sub>x</sub> trap is partially regenerated, thereby substantially preventing slip of NO<sub>x</sub>-specific reactant.

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**GAS TREATMENT USING NO<sub>x</sub>-SPECIFIC REACTANT**

The present invention relates to gas treatment, and more particularly to treatment  
5 of a gas stream containing a NO<sub>x</sub>-specific reactant or one or more nitrogen oxides (NO<sub>x</sub>), especially in an exhaust gas stream of an internal combustion engine.

By "NO<sub>x</sub> specific reactant" herein, we mean a reducing agent that, in most conditions, preferentially reduces NO<sub>x</sub> over other components of a gaseous mixture.  
10 Examples of NO<sub>x</sub>-specific reactants include nitrogenous compounds such as nitrogen hydrides, e.g. ammonia (NH<sub>3</sub>) or hydrazine, or an NH<sub>3</sub> precursor.

By "NH<sub>3</sub> precursor" we mean one or more compounds from which NH<sub>3</sub> can be derived, e.g. by hydrolysis. These include urea (CO(NH<sub>2</sub>)<sub>2</sub>) as an aqueous solution or as a  
15 solid or ammonium carbamate (NH<sub>2</sub>COONH<sub>4</sub>). If the urea is used as an aqueous solution, a eutectic mixture, e.g. a 32.5% NH<sub>3</sub> (aq), is preferred. Additives can be included in the aqueous solutions to reduce the crystallisation temperature.

Urea hydrolyses at temperatures above 160°C according to equation (1) to liberate  
20 NH<sub>3</sub> itself. It also thermally decomposes at this temperature and above according to equations (2) and (3) resulting in reduction of NO<sub>x</sub>.



The NH<sub>3</sub> can be in anhydrous form or as an aqueous solution, for example. Injectors for such reactants or compounds, possibly using carrier gas such as air, have been published. There may be a distinct step of catalytically reacting the precursor to  
30 NH<sub>3</sub>.

In order to meet existing and future emission legislation, generally a vehicular exhaust system includes one or more components, such as catalysts. One of the legislated

exhaust gas components is NO<sub>x</sub>. During normal operation, the exhaust gas produced by a lean-burn internal combustion engine, for example, includes an excess of oxygen and oxidising species. It is very difficult to reduce NO<sub>x</sub> to N<sub>2</sub> in an oxidising or lean atmosphere. In order to treat NO<sub>x</sub> in lean exhaust gases, a component has been developed that absorbs NO<sub>x</sub> during normal lean-burn operation of the engine. This component is commonly called a NO<sub>x</sub>-trap and generally it includes: (i) an oxidation catalyst (e.g. platinum) to oxidise NO in the exhaust gas to NO<sub>2</sub> in the oxidising atmosphere; (ii) a NO<sub>x</sub> storage component to store the NO<sub>2</sub> e.g. as the nitrate. The NO<sub>x</sub> storage component is generally a basic compound of an alkali metal or an alkaline-earth, such as barium oxide; and (iii) a reduction catalyst, such as rhodium. It is possible, however, to use a NO<sub>x</sub> trap formulation in certain circumstances which comprises only the NO<sub>x</sub> storage component, or the NO<sub>x</sub> storage component and one or other of the oxidation and reduction catalyst.

Intermittently, the engine is run rich e.g. by adjusting the moment of fuel injection into one or more cylinders, or a reducing agent is injected into the exhaust gas in order to remove the stored NO<sub>x</sub> and reduce it to N<sub>2</sub>. This also regenerates the absorber for another store-regenerate cycle.

One approach for removing NO<sub>x</sub> from a gas stream is by selective catalytic reduction (SCR), which comprises adding e.g. NH<sub>3</sub> to the gas and passing the mixture over a catalyst effective to react the NO<sub>x</sub> and NH<sub>3</sub> to nitrogen. Another approach is described in our WO 00/21647 wherein NO<sub>x</sub> from a diesel engine exhaust gas is removed by absorbing it in a solid absorbent. The absorbent is regenerated by the action of a NO<sub>x</sub>-specific reactant. Either such process requires careful control to avoid over- or under- supply of e.g. NH<sub>3</sub>, leading respectively to emission of NH<sub>3</sub> or NO<sub>x</sub>. NH<sub>3</sub> is an irritant and has an unpleasant odour and, accordingly, it is undesirable to slip NH<sub>3</sub> to atmosphere. In practice this would mean positioning an oxidation "clean-up" catalyst downstream of the SCR catalyst or NO<sub>x</sub>-trap to oxidise slipped NH<sub>3</sub> to NO<sub>x</sub>. Therefore, slipping NO<sub>x</sub> *per se*, by providing inadequate levels of NH<sub>3</sub>, or NH<sub>3</sub> would have the effect of reducing the overall effectiveness of the exhaust system to limit NO<sub>x</sub> emissions.

We have now discovered that it is possible to regenerate a NO<sub>x</sub>-trap formulation

using a NO<sub>x</sub>-specific reactant, such as NH<sub>3</sub>, whilst substantially preventing slip of NO<sub>x</sub>-specific reactant. In particular, we have found that it is possible to “titrate” the NO<sub>x</sub>-specific reactant against the absorbed NO<sub>x</sub>, whereby addition of NO<sub>x</sub>-specific reactant is stopped before the stored NO<sub>x</sub> is depleted. Thus, stored NO<sub>x</sub> is present to react with the NO<sub>x</sub>-specific reactant thereby to prevent or substantially reduce the likelihood of NO<sub>x</sub>-specific reactant slip. By combining a NO<sub>x</sub> storage component and a catalyst for the reduction of NO<sub>x</sub> using a NO<sub>x</sub>-specific reactant, NO<sub>x</sub> slip can also be reduced or avoided.

This discovery runs counter to the current application of the NO<sub>x</sub>-trap in practice, in that, in our invention, we intentionally avoid substantially regenerating the NO<sub>x</sub>-trap to completeness in order to retain sufficient stored NO<sub>x</sub> to react with NO<sub>x</sub>-specific reactant thereby to prevent slip of the NO<sub>x</sub>-specific reactant. Whilst this observation is of use in vehicle engine exhaust treatment, it also has use in stationary power and chemical plant applications.

Prior documents referred to herein are incorporated by reference.

According to one aspect, the invention provides a process for treating gas containing a NO<sub>x</sub>-specific reactant or NO<sub>x</sub> by contacting the gas with a solid absorbent, which process comprising:

- (a) removing the NO<sub>x</sub>-specific reactant from the gas using a solid absorbent comprising a nitroxy salt; or
- (b) removing NO<sub>x</sub> from the gas using a solid absorbent comprising a basic material and intermittently regenerating the absorbent by the action of a NO<sub>x</sub>-specific reactant and stopping the action of the NO<sub>x</sub>-specific reactant while the absorbent contains nitroxy salt thereby substantially preventing slip of NO<sub>x</sub>-specific reactant.

In a preferred embodiment the intermittent regeneration embodiment of the present invention is carried out in an exhaust system of a vehicle including an internal combustion engine, preferably a lean-burn internal combustion engine.

According to a further aspect, the invention provides an exhaust system for an internal combustion engine, which system includes a NOx-trap disposed in the passage characterised in that the system further includes means for injecting a NOx-specific reactant or a precursor of a NOx-specific reactant upstream of the NOx trap, whereby  
5 NOx stored on the NOx trap is reduced by the NOx-specific reactant and the NOx trap is partially regenerated, thereby substantially preventing slip of NOx-specific reactant.

In one embodiment according to this aspect, the exhaust system further comprises a catalyst for the reaction of NOx with NOx-specific reactant upstream and/or intimately  
10 associated with a NOx-absorbent material component of the NOx-trap, which catalyst is disposed downstream of the means for injecting the NOx-specific reactant.

The system can further include sensors for sensing the presence of e.g. NH<sub>3</sub> downstream of the NOx-trap and a control means, such as the computer of the engine  
15 management unit or a dedicated computer which control means is pre-programmed to control the introduction of NH<sub>3</sub> or precursor into the exhaust passage. For example, the control means can operate in response to the presence or absence of NH<sub>3</sub> (detected by the sensor) downstream of the NOx-trap in order to provide a "negative feed-back loop" arrangement, i.e. when NH<sub>3</sub> is sensed, the control means switches off the supply of NH<sub>3</sub>  
20 or its precursor and *vice versa*.

As defined herein a "solid absorbent", "absorbent" and "absorbent material", "storage component" are used interchangeably; "NOx absorber", "absorber" or "NOx trap" refers to a substrate comprising the solid absorbent, absorbent, absorbent material  
25 or storage component.

In the NOx-removal process at the end of regeneration the absorbent typically contains 5 to 50% of the content of such compounds present at the start of regeneration. To ensure a high level of NOx removal in the absorption phase, the absorbent is not  
30 highly loaded, for example suitably regeneration is started when the absorbent contains 5 to 50% of the NOx content at which NOx absorption ceases.

The process can be carried out batchwise, with a closed vessel containing a body

of gas and a charge of solid nitroxy salt, possibly with relative movement between the gas and salt. More generally applicable is a continuous process, in which a stream of gas flows through the salt or absorbent not yet converted thereto.

5 In a continuous NO<sub>x</sub>-removal process NO<sub>x</sub>-specific reactant feed in the regeneration phase is suitably stopped according to one or more of the following principles:

- (a) when NO<sub>x</sub>-specific reactant is detected partway along the length of the absorber;
- (b) in a system having two or more absorbers in series, when NO<sub>x</sub>-specific reactant is  
10 detected at a point between the absorbers;
- (c) when a level of NO<sub>x</sub> content prescribed by design data, for example on the basis of integration of gas-phase NO<sub>x</sub> flow over time, has been reached;
- (d) when a level of NO<sub>x</sub> content established iteratively (or empirically) from an initial  
15 observation of NO<sub>x</sub>-specific reactant slip has been reached.

Usually the regeneration phase can be a small fraction, e.g. 0.1% to 5%, of engine running time, depending of course on operating conditions. The time frame of absorption and regeneration can be very short, even down to the so-called 'microscopic' scale e.g. of  
20 single engine cylinder strokes or firing order repeats. A suitable range is 1 second to 10 minutes. Accurate and timely supply of NO<sub>x</sub>-specific reactant may be effected by means of a high pressure system analogous to the common-rail system used for engine fuel injection.

The nitroxy salt, absorbent and any catalyst are suitably supported on a ceramic or  
25 metal honeycomb or foam substrate, the ceramic comprising one or more of alumina, silica, titania, cordierite, ceria, zirconia, silicon carbide or other, generally oxidic, material. The honeycomb or foam substrate preferably carries a washcoat and, in one or more layers thereon, the active absorptive and/or catalytic material. The honeycomb has typically at least 50, for example 50-400, cells per square inch (cpsi), possibly more, e.g.  
30 up to 800 cpsi, or up to 1200 cpsi if composed structurally of metal. Generally the range 200-800 cpsi is preferred for the substrate comprising nitroxy salt or absorbent and any catalyst.

The absorbent may be selected from compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitroxy salt (nitrates and/or nitrites) of adequate stability in absorbing conditions and of reacting with NO<sub>x</sub>-specific reactant in regenerating conditions. The “conditions” can include temperature of the gas and its redox state as expressed for example by its lambda; and/or adsorptive materials such as zeolites, carbons and high-area oxides.

Absorbent compounds may be present (before adding nitroxy salt or NO<sub>x</sub> absorption) as composite oxides, e.g. of alkaline earth metal and copper such as Ba-Cu-O or MnO<sub>2</sub>-BaCuO<sub>2</sub>, possibly with added Ce oxide, or Y-Ba-Cu-O and Y-Sr-Co-O. (The oxides are referred to for simplicity, but in practice hydroxides, carbonates and carboxylates such as acetates are present, depending on the temperature and gas composition). Whichever compounds are used, there may be present also one or more catalytic agents, such as precious metals, effective to promote reactions of NO<sub>x</sub>-specific reactant with nitroxy salt. Such catalysts are also known as SCR catalysts and can include iron/zeolite or V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>. Where the NO<sub>x</sub> absorbent and SCR catalyst are associated, in one embodiment they are segregated. By “segregated” we mean that they should, at least, be supported on separate supports and can therefore be disposed in separate layers above and/or below the other component or in the same layer. Alternatively, they can be coated on distinct areas of the same substrate “brick” or on separate substrates disposed within the same system.

Typical gas compositions to be treated by the process are:

(i) NH<sub>3</sub> removal: 1 to 10000 ppm v/v, such as in situations from sewage, toilet and farm effluent gases, to industrial emissions;

(ii) NO<sub>x</sub> removal: 1 to 1000 ppm v/v, such as in internal combustion engine exhausts and industrial emissions;

(iii) Other, major, constituents of such gases include nitrogen, water vapour and carbon dioxide, which generally have little if any unwanted effects on the absorbing material. If strongly oxidising or reducing gases are present in substantial quantities, the absorbent

material should be chosen appropriately; and

(iv) Minor constituents may include for example one or more of CO (up to 500ppm v/v), and hydrocarbon ('HC': up to 500 ppm v/v). The gas can include SOx.

5

If the gas contains SOx, which generally causes loss of activity of the nitroxy compound or NOx absorber, the process may include a SOx absorber upstream of the NOx absorber. Whereas the SOx absorber may be regenerable, e.g. by intermittently subjecting it to high temperature and reducing gas composition, more conveniently the starting gas is of low sulfur content, as from an engine burning fuel of less than 10ppm sulfur; then the SOx absorber can be disposable, and may have sufficient capacity for replacement at the service interval of a vehicle. Since a SOx absorber and a NOx absorber can use the same absorptive material, the replacement procedure can consist in inserting a fresh absorber downstream of the NOx absorber and using the erstwhile NOx absorber as SOx absorber.

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According to an embodiment, the present invention provides an exhaust treatment reactor adapted to such replacement, for example including a module accommodating two absorbers and formed with twin flange means for reverse insertion of the module after replacement of the erstwhile upstream absorber.

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If the NOx of the gas stream to be treated contains NO in excess over NO<sub>2</sub>, the process preferably includes an upstream step of catalytically oxidising NO to NO<sub>2</sub> at least sufficiently to bring NO and NO<sub>2</sub> to molecular equivalence. There may be a step of injecting oxygen if it is not already present in sufficient quantity.

25

If the gas stream contains particulate matter (PM), there may be a step of collecting these by filtration and/or impingement, preferably upstream of the NOx absorber. In the particular case of combustion exhaust gases, especially from internal combustion engines of the lean-burn type such as diesel or GDI, the PM may comprise soot, and then the process includes an upstream step of collecting the soot on a surface (such as of a catalyst) or porous filter. To effect overall continuous removal of such collected soot, an upstream NO catalytic oxidation step should be used, effecting

30

substantially complete conversion of NO to NO<sub>2</sub>. If necessary, the content of NO<sub>x</sub> can be supplemented from an external source, as described for example in EP-A-0341832 or WO 00/74823. Other means of enhancing oxidation may include introducing ozone (WO 99/36162) or plasma (WO 00/21646).

5

In the oxidation catalyst the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with other PGMs, e.g. rhodium, and other catalytic or promoting components. The exact compositions and structure of the oxidation catalyst are not critical to operation of the invention, and hence  
10 may be varied according to the requirements of the situation. A low temperature light-off formulation is generally preferred. Conventional manufacturing techniques may be used. The catalyst should of course be sized and composed to achieve the necessary conversions, and the design should minimise trapping of PM (if present) within its honeycomb substrate.

15

The PM collector/filter may be any capable of trapping the PM without causing excessive backpressure. In general, ceramic, sintered metal or woven or non-woven wire filters are usable, and wall-flow honeycomb structures may be particularly suitable. The structural material of the filter is preferably porous ceramic oxide, silicon carbide or  
20 sintered metal. A coating such as alumina, and also a catalyst such as one or more platinum group metals (PGM) (e.g. Pt with MgO) or La/Cs/V<sub>2</sub>O<sub>5</sub> may be present. The PM is generally soot, mainly carbon and/or heavy hydrocarbons, which are converted to carbon oxides and H<sub>2</sub>O. Certain embodiments of this principle are in commercial use in Johnson Matthey's Continuously Regenerating Trap (CRT™) technology, and are  
25 described in EP-A-0341832 and US 4902487, the teaching of which are incorporated herein by reference.

Regeneration using a NO<sub>x</sub>-specific reactant may be used especially in gases containing oxygen, for example:

- 30 (a) exhaust gas as generated by a lean-burn engine or as issuing from a preceding step of treating such exhaust;
- (b) such gas to which reactant short of equivalence has been or is being added, for example to provide for reaction increasing gas temperature;

- (c) gas made leaner, for example when the reactant is injected with air; or  
(d) rich or equivalent ( $\lambda=1$ ) gas.

The point of injection of the reactant may most simply be just upstream of the absorber; in this event the temperature is typically in the range 150-300°C. However, injection may be earlier; if upstream of a filter but downstream of an oxidation catalyst, the temperature is typically in the range 250-350°C at filter inlet, as required for soot combustion. Further, the reactant may be injected upstream of the oxidation catalyst. Since in such earlier injection the fed reactant is at a 'spike' concentration to react over the short period of regeneration of the absorber, it is in substantial excess over the NO<sub>x</sub> in the flowing exhaust gas and consequently need not suffer much loss by reaction with NO<sub>x</sub>. If in an extreme case it were to react with all the flowing NO<sub>x</sub> to give N<sub>2</sub> or N<sub>2</sub>O, this would stop combustion of soot on the filter: however, owing to the shortness of the NO<sub>x</sub>-specific reactant injection spike, any accumulation of soot would be small and combustion would be resumed before blockage took place. The temperature should not be high enough to give substantial oxidation of e.g. NH<sub>3</sub> to NO<sub>x</sub> over the oxidation catalyst. To limit unwanted side-reactions of e.g. NH<sub>3</sub> it may be introduced as a precursor compound, thus delaying availability of NH<sub>3</sub>. Such limitation may also be provided by suitable formulation of the oxidation catalyst and/or filter. In particular, the filter may be of the non-catalysed type, free of deliberately introduced catalytic material such as PGM. Any fortuitous catalytic activity of the filter, due for example to its structural material or accumulated deposits such as carbon, appears not to seriously promote such side-reactions. If desired, such injection of reactant upstream of an oxidation catalyst can be by way of a non-catalytic sub-region of the honeycomb support of such catalyst, as described in WO 01/96717.

According to a further aspect, the invention provides a system having integers corresponding to the process and also an industrial process plant in combination with the system.

In particular, the invention provides an internal combustion engine (especially a lean-burn engine) including an exhaust treatment system including components for carrying out the process steps corresponding to the process of the invention. The system

may include established expedients such as electric heating or EGR. Such an engine burns fuel preferably less than 50 ppm, especially under 10 ppm, sulfur. For such an engine the process has the substantial advantage over regeneration processes using hydrocarbon that regeneration can take place in lean gas. If the engine includes a high-  
5 pressure system such as common-rail for fuel injection, that system may also actuate  $\text{NH}_3$  injection in  $\text{NO}_x$  absorbent regeneration.

In order that the invention may be more fully understood, the following embodiment and Examples are provided by way of illustration only and with reference to  
10 the accompanying drawings, in which:

Figure 1 is a schematic sectional view of an exhaust treatment system for an internal combustion engine; and

15 Figure 2 is a graph showing the results of % $\text{NO}_x$  conversion over a  $\text{NO}_x$ -trap against time (seconds) at four inlet exhaust gas temperatures.

Referring to Figure 1, the system illustrated consists of single "can" 10, which is connected at 12 to the exhaust from a diesel engine (not shown) fuelled with diesel oil of  
20 under 10 ppm sulfur content. At the inlet end of can 10 is catalyst 14, which is a low temperature light-off oxidation catalyst supported on a 400 cells/in<sup>2</sup> ceramic honeycomb monolith. Catalyst 14 is designed to be capable of meeting emission regulations in relation to CO and HC for the engine and vehicle and also converts at least 70% of the NO in the starting gas to  $\text{NO}_2$ .

25 The gas leaving catalyst 14 passes into soot filter 16, which is of the ceramic wall flow type and collects PM over 50nm. The  $\text{NO}_2$  and surplus oxygen in the gas oxidise the soot at temperatures around 250°C as described in EP-A-341832. The gas leaving filter 16 is passed over sparging spray injector 18, from which it receives intermittent supplies  
30 of  $\text{NH}_3$  or  $\text{NH}_3$  precursor via line 20 from high-pressure pump 22 under the control of computer 24. Computer 24 receives data on engine running time and fuel used, on inlet gas temperature and composition and also, from sensor 26, on any slipped  $\text{NO}_x$  or  $\text{NH}_3$ . It is programmed in particular to recalculate the  $\text{NH}_3$  feed time to a shorter period if  $\text{NH}_3$

is detected in gas leaving absorber 28.

To facilitate replacement of absorber 28, the can portion containing it may be linked to the main upper and lower portion of can 10 by flanges (not shown). If provision for SO<sub>x</sub> absorption is to be made, bed 28 may be in two parts, one upstream of the other, the upstream part being the SO<sub>x</sub> absorber. When the SO<sub>x</sub>-absorbing part is due for replacement, it can be replaced by a fresh SO<sub>x</sub> absorber and the can portion re-inserted with the unreplaced NO<sub>x</sub> absorber in the upstream position.

In the operation of the system two phases alternate. In the absorption phase the gas contains no NH<sub>3</sub> and the NO<sub>x</sub> content of the absorber slowly increases as the NO<sub>x</sub> reacts with the absorbent to give solid nitroxy salt. At the end of this phase the regeneration phase takes place, in which NH<sub>3</sub> is injected until part, suitably 50-90%, or possibly 5-50%, of the nitroxy salt has been reacted. During regeneration the system slips substantially no NH<sub>3</sub> downstream of absorber 28. Stopping injection ends the regeneration phase, so that the absorption phase re-starts with absorption of NO<sub>x</sub> re-starts from its end-level attained in the regeneration phase. If the regeneration phase were continued for longer, for example up to complete decomposition of the nitroxy salt, the NH<sub>3</sub> content of the gas leaving absorber 28 would rise to its level at the start of regeneration, thus emitting NH<sub>3</sub> to atmosphere unless a clean-up catalyst were provided as in conventional continuous SCR.

### **EXAMPLE 1**

A washcoat was prepared using a high shear mixer from 80 parts of gamma alumina (120 m<sup>2</sup> g<sup>-1</sup>) and 20 parts zeolite with sufficient de-ionised water so the final slurry contained 45% solids. A ceramic cordierite monolith (5.66 inch diameter, 6 inch long) having 400 cells per square inch with 6 mm thick wall, was coated by pouring the slurry onto one face and down the channels of the ceramic monolith. Excess slurry was removed from the channels by blowing a jet of compressed air through them. The monolith was then dried in a hot air flow (150°C) for 30 minutes. The dried-coated monolith was then calcined at 500°C for an hour. The total dry washcoat loading on the coated monolith was 2.5 g in<sup>-3</sup>. The monolith was then impregnated with an aqueous solution of barium acetate by immersing it in the solution for five minutes,

removed, and excess metal solution removed by suction. The monolith was then dried in flowing hot air (150°C) and then calcined at 500°C for an hour. The concentration of barium acetate solution was chosen such that the final barium loading on the monolith was 500 g ft<sup>-3</sup> was achieved.

5

A core (one-inch diameter and three inches long) was carefully cut from the monolith using a diamond tipped tool. After wrapping with Fiberfrax™ paper (to prevent gas passing along the outside of the core) it was inserted into a stainless steel housing and placed in a computer controlled test flow reactor equipped with mass flow controllers and gas analysis capabilities before and after the test core. A synthetic gas mixture representative of the exhaust gas from a lean burn internal combustion engine (gas mixture 1 in Table 1) was passed through the monolith core at a steady pre-selected inlet temperature. The following gases were analysed using commercially available analysers: hydrocarbons (HC (Jum Engendering VE7)), carbon monoxide (CO (Unor 6N)), NO<sub>x</sub> (Ecophysics CLD 700 EL), and NH<sub>3</sub> was measured using a tuned infrared laser (Alt Optronic LDS 3000). After being on-line five minutes with gas mixture 1 at an inlet temperature of 150°C, the gas flow was changed to gas mixture 2 (Table 1), that contained NH<sub>3</sub> but no NO<sub>x</sub>. The inlet temperature was kept constant at 150°C, and after 15 5 minutes, the inlet gas was changed again to gas mixture 1 for a further 5 minutes, and the whole sequence was repeated several times.

20

**Table 1. Inlet Gas Mixture Compositions**

Gas Mixture	1	2
Space Velocity	30,000 h <sup>-1</sup>	30,000 h <sup>-1</sup>
CO	200 ppm	200 ppm
25 NO <sub>x</sub>	200 ppm	0 ppm
NH <sub>3</sub>	0 ppm	200 ppm
HC (C <sub>3</sub> )	100 ppm	100 ppm
O <sub>2</sub>	12 %	12%
H <sub>2</sub> O	4.5%	4.5%
30 CO <sub>2</sub>	4.5%	4.5%
N <sub>2</sub>	balance	balance

Typical analytical results obtained are summarised in Table 2 the form of NO<sub>x</sub> conversion at different times after the end of the NH<sub>3</sub> treatment phase. It is clear that NH<sub>3</sub> treatment of the saturated NO<sub>x</sub> absorber regenerated its NO<sub>x</sub> absorbing capability. During the initial part of the NH<sub>3</sub> treatment phase NH<sub>3</sub> was not detected in the exit gas.

**Table 2. Conversion of NO<sub>x</sub> at different temperatures for the barium containing formulation (500 g ft<sup>-3</sup>).**

Temperature	Time after NH <sub>3</sub> treatment	NO <sub>x</sub> Conversion
150°C	5 s	82%
	30 s	75%
	120 s	65%
	300 s	51%
250°C	5 s	88%
	30 s	65%
	60 s	50%
	300 s	25%

### EXAMPLE 2

A NO<sub>x</sub> absorber was made in the same way as described in Example 1, except the barium acetate was replaced by calcium nitrate in the impregnation stage. The concentration of the calcium nitrate solution was chosen to give a final product containing 500 g ft<sup>-3</sup> calcium. Tests as in Example 1 were carried out with an inlet temperature of 165°C, and similar results to those with barium were obtained (Table 3), but at higher temperatures the NO<sub>x</sub> capacity was less than for the barium containing absorber. This may be due to a lower thermodynamic stability of the calcium NO<sub>x</sub> phase, or a lower rate of forming this phase with calcium containing absorber.

**Table 3. NO<sub>x</sub> conversion results at different temperatures for calcium containing absorber formulation (500 g ft<sup>-3</sup>).**

Temperature	Time after NH <sub>3</sub> treatment	NO <sub>x</sub> Conversion
165°C	5 s	70%
	30 s	57%
	120 s	45%
	300 s	38%

**EXAMPLE 3**

5 A NO<sub>x</sub> absorber was made in the same way as described in Example 1, except the barium acetate was replaced by cerium nitrate in the impregnation stage. The concentration of the cerium nitrate solution was chosen to give a final product containing 500 g ft<sup>-3</sup> cerium. Tests as in Example 1 were carried out with an inlet temperature of 165°C, and similar results to those with barium were obtained. The results obtained at inlet temperatures of 165, 350, and 450°C are  
10 displayed graphically in Figure 1. Again it is clear that treatment of the saturated cerium containing NO<sub>x</sub> absorber with NH<sub>3</sub> restored its NO<sub>x</sub> storing capability. At the higher temperatures the NO<sub>x</sub> capacity is significantly less than at lower temperatures, probably because of the lower thermodynamic stability of the NO<sub>x</sub> derived cerium compound at the higher temperatures.

**EXAMPLE 4**

15 A NO<sub>x</sub> absorber was made in the same way as described in Example 1, except the barium acetate was replaced by zirconyl nitrate in the impregnation stage. The concentration of the zirconyl nitrate solution was chosen to give a final product containing 500 g ft<sup>-3</sup> zirconium. Tests as in Example 1 were carried out with an inlet temperature of 165°C, and similar results to those with barium at 150°C were obtained (Table 4). Other results were obtained at inlet temperatures of 250, 350, and 450°C are given in Table 4. Again it is clear that treatment of the  
20 saturated zirconium containing NO<sub>x</sub> absorber with NH<sub>3</sub> restored its NO<sub>x</sub> storing capability. At the higher temperatures the NO<sub>x</sub> capacity is significantly less than at lower temperatures, probably because of the lower thermodynamic stability of the NO<sub>x</sub> derived zirconium compound at the higher temperatures.

**Table 4. NO<sub>x</sub> conversion results at different temperatures for zirconium containing absorber formulation (500 g ft<sup>-3</sup>).**

	Temperature	Time after NH3 treatment	NOx Conversion
5	165°C	5 s	93%
		30 s	86%
		120 s	81%
		300 s	63%
10	250°C	5 s	71%
		30 s	69%
		120 s	60%
		300 s	23%
15	350°C	5 s	81%
		30 s	73%
		120 s	33%
		300 s	29%
20	450°C	5 s	48%
		30 s	42%
		120 s	39%
		300 s	38%

**EXAMPLE 5**

A cordierite monolith (5.66 inch diameter, 6 inch long, 400 cells per square inch with 6 mm thick walls) was coated with a washcoat consisting of gamma alumina (surface area 120 m<sup>2</sup> g<sup>-1</sup>) in water made by slurring sufficient solid in de-ionised water to give a solids content of 45%. The slurry was poured onto the face and down the channels of the ceramic monolith. Excess slurry was removed from the channels by compressed air. The water was then removed from the washcoat by drying in a hot air flow (150°C). The dry coated monolith was then calcined at 500°C for an hour. The total washcoat loading on the coated monolith was 2.5 g in<sup>-3</sup>. The coated monolith was then immersed in a platinum tetra-ammine solution for five minutes, removed, and excess solution removed by suction. The monolith was then dried in a hot air flow (150°C) and calcined at 500°C for an hour. The concentration of solution was chosen to give a platinum loading of 100 g ft<sup>-3</sup> was achieved on the monolith. Next the monolith was impregnated

with an aqueous barium acetate solution. The monolith was immersed in the solution for five minutes, removed, and excess solution removed by suction. The monolith was dried in a hot air flow (150°C) and calcined at 500°C for an hour. The concentration of solution was chosen such that a final barium loading of 800 g ft<sup>-3</sup> was achieved on the monolith.

5

The final monolith was mounted in a stainless steel can using standard procedures, and fitted in the exhaust gas system of 1.9 litre, 4 cylinder turbo-charged diesel engine. The engine was coupled to a dynamometer in the conventional manner. The engine and dynamometer were computer controlled to allow a range of different engine operating conditions to be selected. Exhaust emissions of HC, CO, NO<sub>x</sub>, O<sub>2</sub>, and CO<sub>2</sub> pre- and post-catalyst were measured with commercial gas analysers in the conventional way. NH<sub>3</sub> was measured using a tuned infrared laser (Alt Optronic), and N<sub>2</sub>O was measured with a Unor (Germany) instrument.

10

The engine was operated at 1200 rpm with a dynamometer load of 27 Nm, that resulted in a catalyst inlet exhaust gas temperature of 210°C. The catalyst inlet NO<sub>x</sub> concentration was 160 ppm, and the engine was run steadily at this condition. Every two minutes NH<sub>3</sub> gas was injected into the exhaust upstream of the catalyst in a short pulse. The NH<sub>3</sub> gas level during the injection period was 560 ppm. Initially during NH<sub>3</sub> injection N<sub>2</sub>O was formed in amounts corresponding to that which were formed from the gas phase NO<sub>x</sub> being emitted from the engine, this decreased during the NH<sub>3</sub> reduction of stored NO<sub>x</sub>, presumably as it was absorbed and subsequently reduced to nitrogen. The NO<sub>x</sub> absorption/ NH<sub>3</sub> injection cycle was repeated several times with similar results each time. The NO<sub>x</sub> conversion achieved in a typical period after NH<sub>3</sub> injection is summarised in Table 5. It is clear from these results the NO<sub>x</sub> storing capability of the absorber in the exhaust gas of a Diesel engine is maintained by periodic treatment with NH<sub>3</sub>. The overall NO<sub>x</sub> conversion could be enhanced by suitable optimisation of the system.

20

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**Table 5. Conversion of NO<sub>x</sub> in the exhaust gas of a Diesel engine at 210°C.**

Time after NH <sub>3</sub> treatment	NO <sub>x</sub> conversion
5 s	75%
25 s	63%
50 s	47%
75 s	41%

30

**CLAIMS:**

1. A process for treating gas containing a NO<sub>x</sub>-specific reactant or NO<sub>x</sub> by contacting the gas with a solid absorbent, which process comprising:
  - 5 (a) removing the NO<sub>x</sub>-specific reactant from the gas using a solid absorbent comprising a nitroxy salt; or
  - (b) removing NO<sub>x</sub> from the gas using a solid absorbent comprising a basic material and intermittently regenerating the absorbent by the action of a NO<sub>x</sub>-specific reactant and stopping the action of the NO<sub>x</sub>-specific reactant while the absorbent  
10 contains nitroxy salt thereby substantially preventing slip of NO<sub>x</sub>-specific reactant.
2. A process according to claim 1, wherein at the end of regeneration, the absorbent  
15 contains 5 to 50% of the content of nitroxy salt present at the start of regeneration.
3. A process according to claim 1 or 2, wherein regeneration is started when the absorbent contains 5 to 50% of the nitroxy salt content at which NO<sub>x</sub> slip takes place.
4. A process according to claim 1, 2 or 3, wherein regeneration is controlled to stop  
20 at one of the following points:
  - a. when NO<sub>x</sub>-specific reactant is detected at a point part-way along the length of a substrate carrying the solid absorbent;
  - b. in a system having two substrates carrying the solid absorbent in series, when NO<sub>x</sub>-specific reactant is detected at a point between the substrates;
  - 25 c. when a level of NO<sub>x</sub> content prescribed on the basis of design data has been reached;
  - d. when a level of NO<sub>x</sub> content established iteratively from an initial observation of NO<sub>x</sub>-specific reactant slip has been reached.
- 30 5. A process according to any preceding claim, wherein the time period of absorption and/or regeneration is in the range of from 1 second to 10 minutes.
6. A process according to any preceding claim, wherein the absorbent comprises a

catalyst for the reaction of NO<sub>x</sub> with a NO<sub>x</sub>-specific reactant.

7. A process according to claim 6, wherein the absorbent is supported on a first support and the catalyst for the reaction of NO<sub>x</sub> with NO<sub>x</sub>-specific reactant is supported on a second support.

8. A process according to claim 6 or 7, wherein the catalyst for the reaction of NO<sub>x</sub> with NO<sub>x</sub>-specific reactant is disposed upstream of the absorbent.

9. A process according to any preceding claim including an upstream step of catalytically oxidising NO to NO<sub>2</sub>.

10. A process according to any preceding claim, further including a step upstream of NO<sub>x</sub>-specific reactant-removal or NO<sub>x</sub>-removal of trapping particulate matter on a surface or on a porous filter.

11. A process according to any preceding claim, wherein the NO<sub>x</sub>-specific reactant is produced *in situ* from a precursor thereof.

12. A process according to claim 11, further including a step of catalytically reacting the precursor to provide NO<sub>x</sub>-specific reactant.

13. A process according to any preceding claim, wherein the starting gas is the exhaust of a lean-burn, especially diesel, internal combustion engine.

14. A process according to claim 13, wherein the supply of NO<sub>x</sub>-specific reactant to the solid absorbent is effected by a high-pressure common-rail system.

15. A process according to claim 14 wherein a single high-pressure reservoir feeds both engine fuel injection and NO<sub>x</sub>-specific reactant injection.

16. A process according to claim 13, wherein the engine burns fuel of less than 10 ppm sulfur.

17. A process according to any preceding claim, wherein the NO<sub>x</sub>-specific reactant is ammonia.

18. A process according to claim 11 or 12, wherein the precursor of the NO<sub>x</sub>-specific  
5 reactant is urea.

19. A process according to any preceding claim, wherein absorption and regeneration are conducted under lean conditions.

10 20. A chemical manufacturing process producing waste gas containing NO<sub>x</sub>, including a step according to any of claims 1 to 12.

21. A system for waste gas treatment including items of plant corresponding to a process according to any one of claims 1 to 19.

15

22. A lean-burn internal combustion engine equipped with an exhaust gas treatment system according to claim 21.

23. A chemical plant for any one of aromatics nitration, nitric acid production and  
20 cyclohexane oxidation including a system according to claim 21.

24. An exhaust system for an internal combustion engine, which system includes a NO<sub>x</sub>-trap characterised in that the system further includes means for injecting a NO<sub>x</sub>-specific reactant or a precursor of a NO<sub>x</sub>-specific reactant upstream of the NO<sub>x</sub> trap, whereby NO<sub>x</sub> stored on the NO<sub>x</sub> trap is reduced by the NH<sub>3</sub> and the NO<sub>x</sub> trap is partially regenerated, thereby substantially preventing slip of NO<sub>x</sub>-specific reactant.  
25

25. An exhaust system according to claim 24, further comprising a catalyst for the reaction of NO<sub>x</sub> with NO<sub>x</sub>-specific reactant upstream and/or intimately associated with a NO<sub>x</sub>-absorbent material component of the NO<sub>x</sub>-trap, which catalyst is disposed downstream of the means for injecting the NO<sub>x</sub>-specific reactant.  
30

26. An exhaust system according to claim 24 or 25, wherein it is a lean-burn internal combustion engine.

27. An exhaust system according to claim 26, wherein the lean-burn internal  
5 combustion engine is a diesel engine or a gasoline direct injection engine.

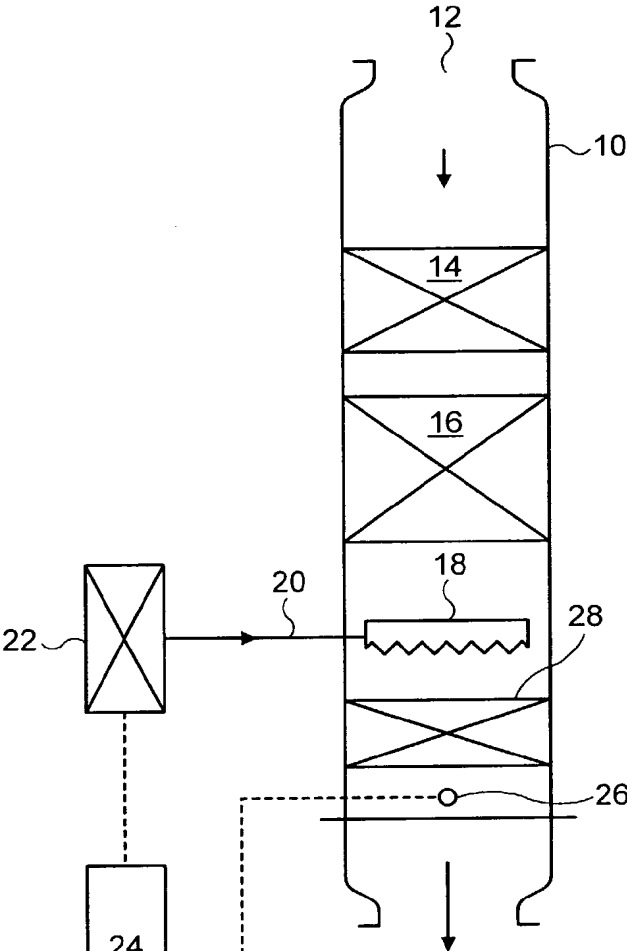


FIG. 1

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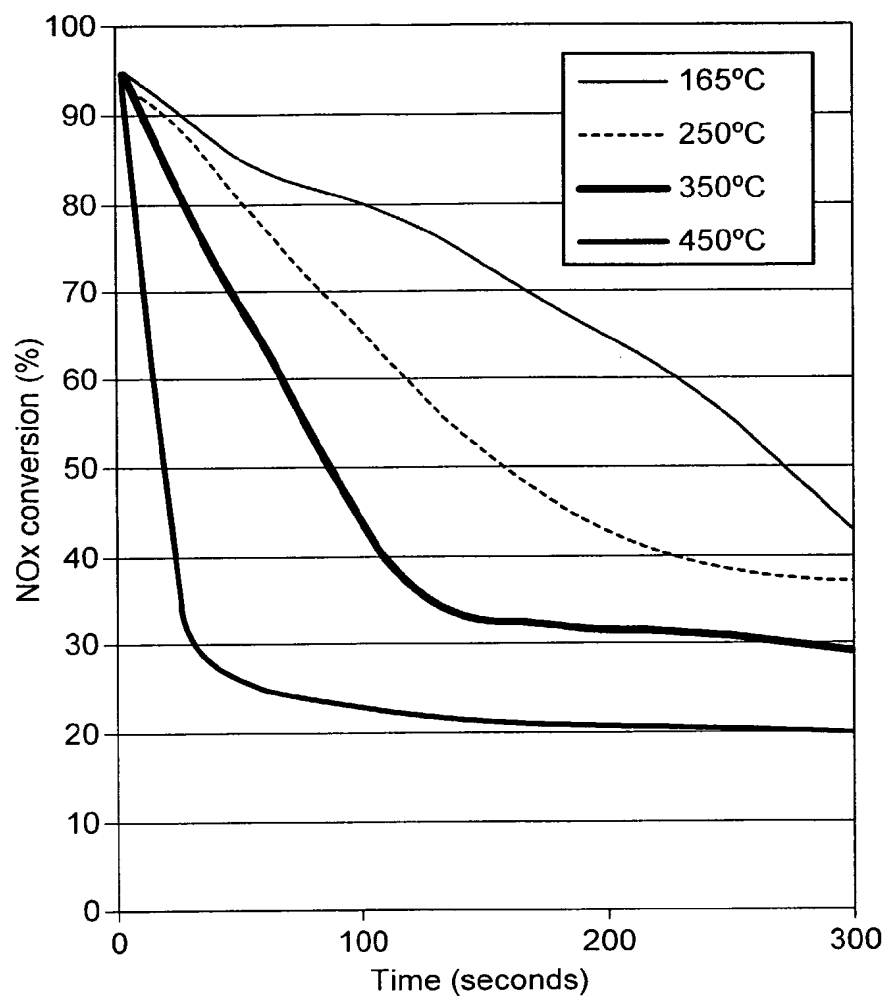


FIG. 2

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/00784

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/94 F01N3/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 21647 A (JOHNSON MATTHEY ) 20 April 2000 (2000-04-20) cited in the application the whole document ---	1-27
A	US 6 125 629 A (JOSEPH A. PATCHETT) 3 October 2000 (2000-10-03) ---	
A	US 6 092 367 A (WINFRIED DÖLLING) 25 July 2000 (2000-07-25) -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Intel<sup>®</sup> Patent Application No  
PCT/GB 02/00784

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 0021647	A	20-04-2000	AU	6111799 A	01-05-2000
			EP	1128895 A1	05-09-2001
			WO	0021647 A1	20-04-2000
<hr/>					
US 6125629	A	03-10-2000	AU	2146200 A	05-06-2000
			EP	1129278 A1	05-09-2001
			WO	0029728 A1	25-05-2000
<hr/>					
US 6092367	A	25-07-2000	DE	19536571 A1	10-04-1997
			AT	198096 T	15-12-2000
			CN	1198796 A	11-11-1998
			WO	9713055 A2	10-04-1997
			DE	59606224 D1	18-01-2001
			DK	852661 T3	17-04-2001
			EP	0852661 A2	15-07-1998
			ES	2153605 T3	01-03-2001
			JP	11512799 T	02-11-1999
<hr/>					